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Electroanalysis of nitrobenzene derivatives and nitrite ions using silver nanoparticles deposited silica spheres modified electrode

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A B S T R A C T

An electrochemical sensor was developed for the detection of nitrobenzene derivatives and nitrite ions using silver nanoparticles (Ag NPs) deposited on amine functionalized silica (SiO_2) spheres modified electrode. The electrocatalytic reduction of nitrobenzene and oxidation of nitrite ions were studied using SiO_2/Ag NPs at three different Ag concentrations (1, 2 and 3 mM) modified electrodes. In electrocatalysis, a positive shift in the reduction peak potential for nitrobenzene and a significant increase in the catalytic oxidation current for nitrite ions were observed at these modified electrodes. An improved electrocatalytic activity for the reduction of nitrobenzene and oxidation of nitrite ions was achieved at the SiO_2/Ag (3 mM) NPs modified electrode due to the large number of Ag NPs deposited on SiO_2 surface. The lowest experimental detection limits of 500 nM for nitrobenzene derivatives and 1 μM for nitrite ions at the SiO_2/Ag NPs modified electrode were observed.

1. Introduction

Nitroaromatic compounds are mutagenic and carcinogenic substances that create toxic effects for human health [1,2]. Therefore, the detection of these compounds has gained more attention in the field of sensing of toxic molecules. Explosives, herbicides, insecticides and leather industries provide a major source for the extensive release of these nitroaromatic compounds [3,4]. The strong electron withdrawing tendency of nitro group present in nitrobenzene and its derivatives reduces the electron density of benzene ring and makes them stable. This makes the nitrobenzene and its derivatives as one of the stable and polluting compounds when they enter the soil or water. Many research groups have developed electrochemical sensors for the detection of nitroaromatic compounds and the electrochemical technique is advantageous due to its easy operation, sensitivity, response time and low-cost fabrication [5–9]. Our group has reported the electrochemical sensors for the detection of nitrobenzene and nitrobenzene derivatives using silver (Ag) nanoparticles (NPs) [10,11], gold (Au) NPs [12] and the electrocatalytic reduction of nitrobenzene using Au/Ag bimetal nanorods [13] modified electrodes.

The detection of nitrite ions is one prime area of research due to their toxicity and their ability to form carcinogenic nitroso-amines in human stomach through food chain [14–16]. Nitrite ions contaminated water creates shortness of breath and blue baby syndrome when it is consumed by children [17,18]. So the designing of sensors for the detection of nitrite ions is very important. According to the World Health Organization, nitrite ions should have a guidance level of 65 μM for short-term exposure and a provisional guidance level of 4.3 μM for long-term exposure [19]. Some interesting electrochemical sensors were developed in recent years for the detection of nitrite ions using a copper oxide–graphite composite electrode [20], ferricyanide–poly(diallyldimethylammonium)–alginate composite film [21], electropolymerized film of functionalized thiadiazole modified glassy carbon electrode [22], thionine modified aligned carbon nanotubes [23] and shallow recessed screen printed microelectrode arrays [19]. Our group has reported the electrochemical sensing of nitrite ions using Au NPs [24] and Au/Ag bimetal nanorods [25] modified electrodes. The electrochemical detection of nitrite ions can be carried out either by oxidation or reduction. The oxidation of nitrite ions offers many advantages like no interference from nitrate ions and from dissolved molecular oxygen [26,27].

Metal NPs with different shape and size have been the focus of intense research in recent decades due to their unique physical, chemical properties and their applications in catalysis and sensors. The development of different synthetic methods for the preparation of metal NPs encapsulated by silicate sol–gel (SSG) matrix is an emerging field since they exhibit a wide range of applications in catalysis and sensors [10,11,28]. The metal NPs supported on silica (SiO_2) spheres are used for optical [29,30] and electrocatalytic

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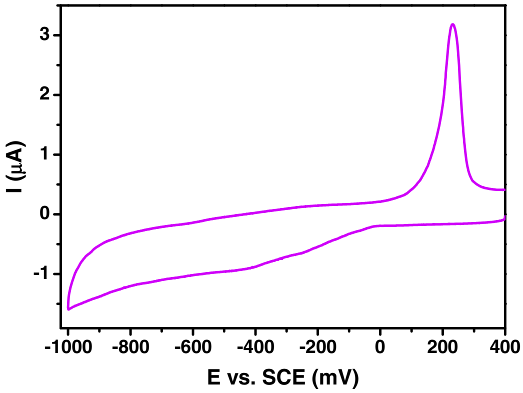

Fig. 1. Cyclic voltammogram recorded for GC/TPDT–SiO_2/Ag (3 mM) NPs modified electrode in 0.1 M PBS (pH 7.2) at a scan rate of 50 mV s^{-1}.

[31,32] applications due to the higher active surface area provided by the SiO_2 spheres. In particular, Ag NPs embedded with SSG matrix or supported on SiO_2 find interesting applications in catalysis and sensors [10,11,29,30,33]. For the detection of toxic molecules, Ag NPs based modified electrodes are promising due to its low cost when compared to Au, Pt and Pd.

Herein, we report an electrochemical sensor for the detection of nitrobenzene derivatives and nitrite ions using silver nanoparticles (Ag NPs) deposited on amine functionalized silica (SiO_2) spheres modified electrodes. The electrocatalytic reduction and oxidation of nitrobenzene and nitrite ions respectively, were studied at the SiO_2/Ag NPs with three different Ag concentrations (1, 2 and 3 mM) modified electrodes. The improved electrocatalytic activity of SiO_2/Ag NPs (3 mM) modified electrode was achieved in both the cases. The lowest experimental detection limits for the sensing of nitrobenzene derivatives and nitrite ions at SiO_2/Ag NPs modified electrodes were found to be 500 nM and 1 µM, respectively.

2. Experimental

2.1. Materials and instruments

Tetraethylorthosilicate (TEOS), *N*-[3-(trimethoxysilyl)propyl] diethylenetriamine (TPDT), silver nitrate ($AgNO_3$), β-cyclodextrin (CD), benzyldimethylhexadecylammonium chloride (BDAC) were received from Sigma–Aldrich. Ascorbic acid (AA), sodium nitrite, sodium dihydrogen phosphate and disodium hydrogen phosphate were purchased from Merck. Nitrobenzene, *p*-nitrotoluene, *p*-nitrobenzoic acid, *p*-nitrophenol and *p*-nitroaniline were received from SRL. All glassware was thoroughly cleaned with aqua regia (*Precaution: Aqua regia is highly corrosive and it should be handled with care.*) and rinsed extensively with doubly distilled water before use. The electrochemical measurements were performed at room temperature using CH Instruments Electrochemical Workstation (model-760D).

2.2. Synthesis of SiO_2/Ag NPs

The amine functionalized SiO_2 spheres were prepared by modified Stober method using TPDT silane [31]. Briefly, ammonium hydroxide (1.7 mL; 25–28%) was added to ethanol (50 mL) along with TEOS (1.5 mL) and water (1 mL) under vigorous stirring. After 3 h, an additional 1 mL of TEOS was added into the above mixture. The SiO_2 spheres were formed as colorless precipitate after 12 h of stirring. For amine functionalization, TPDT (0.4 mL) was added to the solution and the stirring was continued for further 6 h. The TPDT functionalized SiO_2 particles were purified twice by centrifugation and redispersed in water (40 mL). The SSG matrix encapsulated SiO_2/Ag (1, 2 and 3 mM) NPs were prepared as reported earlier [30]. Briefly, 25 µL of 1 M TPDT silane was added to 5 mL pre-stirred aqueous mixture containing each 7 mM β-cyclodextrin (CD) and BDAC and then further stirred for 1 h. To this β-CD–TPDT–BDAC composite, 5 mg of preformed amine functionalized SiO_2 was added and sonicated for 5 min. To this resulting solution, 50 µL of 0.1 M $AgNO_3$ and 50 µL of 0.1 M AA were added. The appearance of yellowish orange color solution indicated the formation of Ag NPs.

2.3. Electrochemical measurements

The electrochemical measurements were carried out using a single compartment three-electrode cell. The working electrode was prepared by drop casting 5 µL of TPDT–SiO_2/Ag NPs solution on a glassy carbon (GC) electrode surface (3 mm dia.) and dried at room temperature. The GC electrode was cleaned by polishing twice with alumina (0.05 micron) and by potential cycling between +1 and −1 V in 0.1 M H_2SO_4 before use. A calomel electrode and a platinum wire were used as reference and counter electrodes, respectively. The electrochemical measurements were performed at room temperature (25 °C) using CH Instruments Electrochemical Workstation (model-760D) in deaerated 0.1 M phosphate buffer solution (PBS) (pH 7.2). The square wave voltammetric measurements were carried out with a step potential of 4 mV, amplitude of 25 mV, and a frequency of 25 Hz.

3. Results and discussion

The detailed characterization of SiO_2/Ag NPs was provided in our previous report [30]. The TEM image of SiO_2/Ag (3 mM) NPs

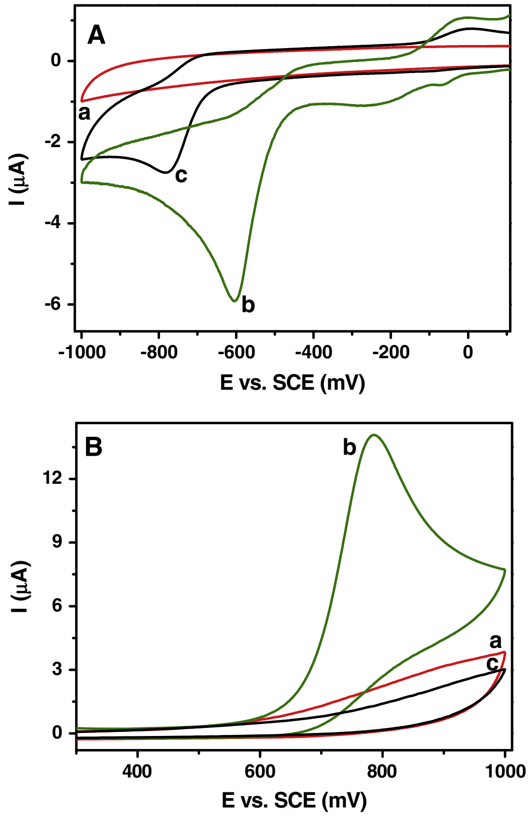

Fig. 2. Cyclic voltammograms recorded at GC/TPDT–SiO_2/Ag (3 mM) NPs modified electrode in the absence (a) and presence (b) of each 100 µM nitrobenzene (A) and nitrite ions (B), respectively in 0.1 M PBS (pH 7.2) at a scan rate of 50 mV s^{-1}. (c) Cyclic voltammograms recorded at bare GC electrode in the presence of nitrobenzene (A) and nitrite ions (B).